COMPLETE SPECIFICATION.

A Process for the Production of Carboxylic Acids.

We, ETHYL CORPORATION, a Corporation organised under the laws of the State of Virginia, United States of America, of 330 South Fourth Street, Richmond, State of 5 Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the follow-10 ing statement:—

This invention relates to a process for the production of carboxylic acids and in particular to the preparation of carboxylic acids by the partial oxidation of hydrocarbon ma-15 terials. The term "hydrocarbon materials" as used in the specification and claims means saturated and unsaturated hydrocarbons, which may be cyclic, non-cyclic, or branched chain, and with or without substituents, the 20 aromatic hydrocarbons, with or without substituents.

Hydrocarbons have heretofore been subjected to oxidation with an oxygen containing gas, in an effort to attain carboxylic acids. 25 However, because of various factors, the desired products have not been obtained in high yields or purity, but have included undesired compounds such as hydroxy acids, keto-acids, keta-alcohols, and polyols. High 30 boiling impurities have been found which are believed to result from the esterification of hydroxyl groups by high molecular weight acids produced. High molecular weight esters are disadvantageous because they are diffi-35 cult to hydrolyze to recoup the acid values.

We have now found that carboxylic acids may be produced in improved yields by the oxidation of hydrocarbons in the presence of a mixture of acetic and propionic acids. It 40 will be understood of course that the acids are those not normally present in the reaction mixtures to which they are added.

According to the present invention there

[Price 4s. 6d.]

is provided a process for the production of aromatic or aliphatic carboxylic acids, which 45 process comprises oxidising a hydrocarbon material with an oxidant comprising gaseous oxygen, in the presence of a mixture of propionic acid and acetic acid, either added to the hydrocarbon material or formed in situ, 50 which mixture forms a single phase liquid system with the hydrocarbon material.

It is thought that a single phase liquid system is extremely important for securing enhanced oxidation of intermediates such as 55 hydroxyls and carbonyls to acid. There is a marked synergism with a reaction medium or system that contains a strong organic acid with an oxidation inert coordinator for water and hydrocarbon phases whether or 60 not such phases actually exist or could exist otherwise. The only lower acid that alone can fulfill both requirements to any substantial degree is propionic, and this by itself is generally inferior to a synergistic 65 combination. A combination of acetic and propionic acids provides a synergistic result. A coordinated oxidation mixture has all the appearances of a true solution, being clear, free of stratification or of the opacity 70 characteristic of emulsions. Such a mixture will readily oxidize at temperatures which are substantially lower than systems which are not coordinated. Acetic acid has little if any coordination capability. 75

As can be seen from the Examples below the use of a mixture of acetic and propionic acids gives a rapid oxygen uptake rate at lower temperatures. With conversion to oxygenated molecules at about 25 percent in 80 comparison to conventional oxidation there is easily achieved a factor-of-3 reduction in hydroxyl number, carbonyl value and ester value. The lactones are reduced by a factor-of-7. Molecular length degradation of pro-85 duct acids relative to starting hydrocarbon is

greatly reduced, the quantity of high molecular weight acids is increased by 50 percent or more. It is even possible to produce adipic acid at high yield by the oxidation of cyclohexane in a single air oxidation stage.

One important aspect of the process of the present invention is that it is conducted in a mode which is not limited by oxygen availability or lack of it. In other words once an attack occurs it is desired to have adequate oxygen available to complete the oxygenation to acid of any molecular "ends" involved. Since oxygenation to CO_2 would occur with unlimited oxygen availability unless some other control were provided, it has been found that a temperature limited mode of operation is highly effective to enhance the production of acid. Thus the great significance of temperature becomes apparent and since new attacks on molecules appear to increase disproportionately to completion of attack as operation goes to higher temperatures, it is desired to maintain the temperature of the reacting material as low as possible at all times when oxygen is available. Therefore where it is possible to oxidize straight chain materials at 115°C. and cyclic materials at 106°C., it is preferred to maintain the temperature near such marginal points.

In general the oxygen concentration in the oxidizing gas is maintained preferably at about 14 volume percent concentration to secure oxygen availability for conversion of cleavage products to acid. The reaction is preferably carried out at pressures of from 3 to 25 atmospheres. Operating temperatures may be varied but the lowest temperature consistent with reasonable reaction rate are desired. Suitable temperatures are from about 106°C to 115°C.

Pure oxygen or oxygen enriched air may be used, but to avoid the danger of explosion it is preferred to use air as the oxidant.

An oxidant comprising oxygen diluted with materials other than nitrogen may also be used, for example, oxygen diluted with CO_2. Actually at the higher pressure involved when such a diluent is used, such as 250 psig, there appears to be a decarboxylation retardant effect, such as an equilibrium, when CO_2 contributes to the "inert" or non-oxygen content of the oxidizer system. This may be obscured in a continuous system where the off-gases are recirculated, but is evidenced in a batch operation by deliberately adding CO_2 to the reaction environment at the start.

The process of the present invention may be carried out in the presence of a suitable catalyst, preferably the carboxylate of a heavy metal such as manganese stearate.

The process of the invention may be used to oxidise a wide range of hydrocarbon materials, and is especially suitable for oxidis-

ing pure straight chain hydrocarbons of singular molecular weight or mixtures of straight chain hydrocarbons of mixed molecular weight averaging about 5 carbon atoms per molecule higher than the average number of carbon atoms desired in the product acids.

The process of the present invention may also be used to oxidise cyclic hydrocarbons, and in a preferred embodiment there is provided a process for producing adipic acid which process comprises oxidizing cyclohexane with an oxidant comprising gaseous oxygen in the presence of a mixture of acetic acid and propionic acid, the mixture forming a single phase liquid system with the cyclohexane, and the volume of the propionic acid present being at least equal to the volume of the acetic acid present, said oxidation being conducted under a pressure of from 3 to 25 atmospheres and in a temperature limited mode with excess oxygen available, distilling the oxidate under non-oxidizing conditions at a temperature above the melting point of adipic acid to remove cyclohexanol, cyclohexanone and lower boiling materials, recovering the molten adipic acid, and recycling at least a part of the distillate to oxidation.

The adipic acid produced by the process of this embodiment may be used to prepare nylon by a condensation reaction with hexamethylene diamine. The invention includes such a polymer when prepared from adipic acid produced by a process in accordance with the invention and hexamethylene diamine on an condensation reaction.

It is preferred that the proportions by volume of the hydrocarbon material, the propionic acid and the acetic acid be about 25:15:10.

A vast improvement is realized when the coordination concept is applied in oxidations where the material oxidized is miscible with acetic acid.

The post-treatment of the oxidate of processes of the invention and recovery of acids therefrom is a surprisingly simple matter, far easier than that with prior art oxidates, because of the low content of highly troublesome hydroxyls, carbonyls, esters and lactones. The boiling points, melting points and solubilities of the particlar materials involved require some variation in individual processing. As an example where hexadecane is oxidized to produce C_{16} to C_{10} monobasic acids the lower acids may be removed by a simple distillation and water wash and the resulting oxidate mildly hydrogenated to hydrolyze esters and remove non-carboxyl oxygen. The resulting material is then treated with a saponification agent to separate unsaponifiables for recycle to oxidation. The acids may be sprung and used

without further treatment since they usually have 90 percent or higher purity.

Several rules of thumb have been developed as to quality of oxidation. A ratio of Acid Value to Ester Value in crude acid sprung from soaps without intervening hydrogenation is considered good when it is 10:1 or better. This is now easily achieved in the present process but virtually impossible in the prior art when dealing with the preparation of acids in the 10—16 carbon atoms per molecule range. Another criteria is low carbonyl value. Values below 1 are readily attainable here but difficult with the prior art.

A hydrogenation treatment of crude acids which involves simultaneous hydrolysis of esters and dehydration of secondary hydroxyls is a compromise proposition because effective hydrolysis in general requires the presence of water whereas effective dehydration of secondary alcohols requires a near anhydrous environment. Furthermore esters of 20 and more carbon atoms per molecule are quite hydrophobic and are not readily hydrolyzed unless some provision is made for securing enhanced contact thereof with water. It has been found that the lower acid coordination system employed in oxidation may be used to advantage in hydrogenation and that rather than adversely effect the ester hydrolysis equilibrium as would normally be expected, by its inherent water coordination nature and high activity it enhances hydrolysis of esters and lactones of intermediate and higher acids that happen to be present as well as of polyesters causing them to liberate equilibrium quantities of secondary hydroxyl components from the esters that are involved, as well as hydroxyl groups of hydroxy acids where that type of configuration is involved, permitting the release of such hydroxyl groups to dehydration which is followed by saturation of resultant unsaturated linkage.

From the foregoing it is readily appreciated that with proper treatment of oxidate the formation of high boiling residue may be significantly reduced and simple hydrogenation of oxidate made possible to produce saturated carboxyl only acids of 95 percent or better purity in a single stage to an extent that requires five or more similar consecutive stages with oxidate produced by prior art techniques.

In the course of experimentation, vapour phase chromatography was employed for the analysis of samples was preceded by the conversion of acids into methyl esters by several techniques of esterification. One employed BF_3 and methanol. Another esterification used diazo methane. Paraffins, ketones, olefins, secondary alcohols and the like are not esterified and remain in the sample to exhibit their own characteristics.

A typical vapour phase chromatography chart derived in analysis of the product of a non-acid additive oxidation of pure hexadecane is represented in Figure 2, of the accompanying drawings containing "peaks" 6, 7, 8, and 9 which indicate the methyl esters of monocarboxylic acids having 6, 7, 8, and 9 carbon atoms per molecule, respectively. Each of these peaks is followed by a stair step of significant amplitude and duration. Peak 10 is of large amplitude and corresponds to unreacted hexadecane. The step following peak 9 is believed to be hydrocarbon of 15 carbon atoms per molecule, that following peak 8 is hydrocarbon of 14 carbon atoms per molecule and so forth. In contrast, a chart showing analysis of a product resulting from an oxidation in an acid additive coordinated system is shown in Figure 1 of the accompanying drawings. In this chart the almost complete absence of the stair-steps following the same methyl esters indicated by reference characters A6, A7, A8 and A9 is to be noted.

Turning now to the portion of the analysis representations in the region of the indications for the monocarboxylic acids having 11, 12, 13 and 14 carbon atoms per molecule, it is noted in Figure 2 that either the VPC baseline has shifted for some unknown reason and indicates small quantities of these acids or the baseline is correct and there are vast quantities of impurities between the peaks identified as the acids (in methyl ester forms). In comparison, Figure 1 shows larger quantities of the acids (methyl esters) and far less intervening impurity. The nature of many impurities in the non-acid oxidation system has not been determined with certainty despite the fact that many oxidations have been conducted and hundreds of VPC analyses made. However, it is believed that these are several series of isomeric difunctional molecules such as hydroxy acids, lactones or unsaturated acids or polymers of unsaturated acids and if this is the case their absence from the traces of Figure 1 is of considerable significance because this may indicate that the formation of these precursors of the troublesome polyesters may be significantly reduced. Whatever the actual nature of these impurities happens to be however, it is important to note that these are missing almost entirely from the analysis chart of the product of an acid additive coordinated oxidation system in accordance with the invention as shown in Figure 1.

In comparing Figures 1 and 2, attention is directed to the indications of the presence of substantial quantities of materials boiling above the methyl ester of tetradecanoic acids in both traces. Two of these peaks are tentatively identified as pentadecanoic acid and hexadecanoic acid. Others are believed to be largely ketones and secondary alcohols.

The significant feature in any event is that the quantity of these materials is significantly lower in acid additive oxidation in comparison to non-additive oxidation.

A reduction in the hydroxyl content of the oxidate obtained in acid additive oxidation was one of the improvements sought in making the present invention. However, the magnitude of the reduction relative to the ester value increase for Examples 1 and 2 below was totally unexpected. Although the hydroxyl percentage of Example 1 was reduced to one-half of the value experienced in non-additive oxidation, the ester value increased by a mere 10 percent. It is recognized that these ratios are not comparable quantitatively because other factors are involved but it is indicative of a 5 for 1 alteration. Each additional molecule of ester produced in the oxidate as a result of the propionic acid presence withdraws several hydroxyl groups from those available for other esterification of a more adverse nature, namely the production of esters of C_{11} to C_{15} acids or of polyesters.

An incidental benefit of acid additive oxidation is that adverse effects of polyfunctional molecules in the oxidate or in the oxidation mixture during the reaction is reduced considerably since the hydroxyl groups are tied up as acetates or propionates making it possible to employ a higher percentage conversion of original hydrocarbon to oxygenated molecules. For example, polyesters based on hydroxy acids are no longer a limiting factor so that dibasic acid production and permissible cleavage provide the principal remaining limitations to high conversion to produce monobasic acids.

A matter of considerable significance is the low temperature at which excellent oxidation rates are experienced, typically 115°C. for straight chain materials such as hexadecane and octadecane and mixtures of such materials, such as those from C_{16} to C_{20}, while cyclic materials such as cyclohexane oxidize readily even at 106°C. At these temperatures corrosion problems are quite minor and numerous readily available plastic coatings of low cost are entirely suitable. These coatings are believed to be an important factor in obtaining high purity of product and have been given extensive testing under actual operating conditions with excellent results even when applied to mild steels.

Following is a description by way of example to further illustrate processes in accordance with the invention. Example 2 is comparative.

EXAMPLE 1

A mixture of 236 grams of hexadecane, 129.2 grams of propionic acid and 72.2 grams of acetic acid (250 : 150 : 100 vol ratio) was oxidized with air at a temperature of from

114 to 119°C., and at a pressure of 250 psig for 5 hours using 1 percent manganese stearate catalyst. The percentage of O_2 in the off-gas was 14.5 percent. The oxidate weighed 442.5 grams. The oxidate was then subjected to a flash operation wherein 210.6 grams of acetic and propionic acids were removed leaving 229.4 grams of acid materials. The acid materials were washed with water after which 218.4 grams remained. This was then saponified with alcoholic KOH (2N) yielding 160.4 grams of soaps. These soaps were washed with pentane to remove residual hydrocarbons and then distilled with concurrent addition of water to remove the methyl alcohol used in saponification, accomplishing hydrolysis of any methyl esters that might exist. The soaps were treated with 157.4 grams of 2N H_2SO_4 and 128.3 grams of water to spring the acids. Acids sprung were then washed with water to yield 29.6 grams of crude acid. VPC recovery of the crude acids was 62 percent, miscellaneous 13.5 for an excellent total VPC recovery of 75.5. Wet chemical analyses of the crude acid showed an Acid Number (conventional measurement) of 258, Ester Value of 26.0, carbonyl value 0.43. The crude acid contained 0.86 percent C_5 acid; 3.67 percent C_6 acid; 5.83 percent C_7 acid; 7.27 percent C_8 acid; 8.19 percent C_9 acid; 9.58 percent C_{10} acid; 9.30 percent C_{11} acid; 7.38 percent S_{12} acid; 5.66 percent C_{13} acid; 2.60 percent C_{14} acid; 0.36 C_{15} acid; and 1.26 percent C_{16} acid. The C_{11}—C_{16} acid was 26.56 percent of the total acid.

The crude acids were then hydrogenated at 210°C. and 400 psig for 2 hours using a nickel-clay catalyst. The VPC recovery of the hydrogenated acids was 95 percent.

In Examples 2 to 10 below the general technique of Example 1 was used, but the results are only partially listed for comparative purposes. These Examples were selected to show certain effects particularly VPC recovery and other quality criteria as a function of different variables. Overall oxidations were sought to be made equal by operation at a constant air flow rate for the same duration (300 minutes) with a constant oxygen content of the off-gas of from 14 to 17 percent. In general the total oxygen uptake was uniform at from 14 to 15 grams oxygen pick-up to produce a conversion of 8 to 12 percent of hydrocarbon charged. Temperature was adjusted to maintain the desired rate of oxygen and hence a direct indication of effect on oxygen take up rate, and lower temperatures were preferred. Some runs were made using recycle unsaponifiable material from previous runs. This contained 125 approximately 95 percent C_{16} alkane, 3 percent C_{16} ketone and 2 percent C_{16} secondary alcohol with no lactone or ester content.

Catalyst and initiation were noteworthy

details. At atmospheric pressure and without the acetic-propionic acids system, an induction period was necessary in which the material was heated to 140°C. for approximately 5 minutes before the temperature could be lowered without stopping the oxidation. In the pressure acid additive system with either fresh paraffin feed with either type catalyst represented by tertiary butyl hydroperoxide or manganese stearate or with no catalyst using recycle material in which the very components apparently act as catalysts, no induction period involving "superheating" was required so that the oxidate never had a high temperature history. It is believed that high temperatures produce a disproportionate quantity of attacks per molecule and thereby contribute materially to the formation of the undesired materials.

EXAMPLE 2

Example 1 was repeated using hexadecane at atmospheric pressure without acid additive to develop a comparative feel on oxidation temperature. Tertiary butyl hydroperoxide catalyst was used. Oxidation temperature of 142°C was required.

EXAMPLE 3

Example 1 was virtually duplicated as to conditions of oxidation except acetic anhydride was substituted for acetic acid. The volume proportions were 300:167:33. Results were similar with the crude acid showing an acid recovery of 60.2 percent, miscellaneous 19.27 for an excellent total 79.43. The wet chemical analysis showed an Acid Number of 257, Ester value of 45.4, Carbonyl value 0.56, hydroxyl value 2.39.

EXAMPLE 4

The basic technique of Example 1 was followed using hexadecane, propionic acid and acetic acids in 250:150:100 volume relationship at 250 psig using 1 percent manganese carboxylate catalyst. VPC recovery of the oxidate after lower acid flash and water wash was 63.5 percent acids, 12.5 percent miscellaneous for an excellent 76 percent total. Oxidation temperature was 120°C.

EXAMPLE 5

This Example was virtually a duplicate of Example 4 using recycle C₁₆ material without catalyst at 100 psig. VPC recovery was 57 percent acids, 16 percent miscellaneous for a total of 73 percent.

EXAMPLE 6

This Example was virtually a duplicate of Example 5 except that a pressure of 250 psig was used. VPC recovery was 55 percent acids, 19 percent miscellaneous for a total of 74 percent. The temperature was 117°C.

EXAMPLE 7

Example 1 was repeated using 1 percent tertiary butyl hydroperoxide catalyst instead of manganese stearate. VPC acid was 59.5 percent, miscellaneous 8.5 for a total recovery of 67.9 percent. Acid number was 247, Ester value 32.3, carbonyl value 1.08.

EXAMPLE 8

The technique of Example 1 was followed with octadecane, propionic acid and acetic acid in 250:150:100 ratio at 250 psi. 117°C. using 1 percent tertiary butyl hydroperoxide catalysts. Wet analysis showed Acid number 216, Ester value 48.1, carbonyl 1.29, hydroxyl 1.07, iodine number 14.9.

EXAMPLE 9

The oxidation of Example 8 was repeated using 1 percent manganese stearate catalyst at 117°C. The oxidate contained 11.6 percent acid after the flash and water wash removal of lower acids. The VPC recovery of this was 60 percent acids, 15 percent miscellaneous, for an excellent total recovery of 75 percent. Of the 60 percent VPC acids, 54.7 percent fell in the C₁₁—C₁₆ range. The wet analysis was Acid number 227, Ester value 24.0, and carbonyl value 0.60. The oxidate after flash and wash was then mildy hydrogenated (210°C., 400 psi, 2 hours, nickel-clay catalyst). The product was saponified, separated and sprung to yield acids having VPC analysis of 93 percent acids in which 62 percent were in the C₁₁—C₁₆ range. This marked a 14 percent increase in the C₁₁—C₁₆ acids, presumably the result of recovery of such acids from the esters.

EXAMPLE 10

Example 9 was repeated using octadecane and propionic acid in 1:1 volume ratio at 250 psig with 1 percent tertiary butyl hydroperoxide catalyst. A temperature of 140° was required however a high acid content of 26.5 percent was noted in the oxidate after flash and water wash of the lower acids. VPC recoveries were much poorer, 47.69 percent acid, 3.29 miscellaneous for a total of 50.98. Acid value was somewhat low at 218, Ester value 56.5, carbonyl 1.31, hydroxyl 1.67.

EXAMPLE 11

Example 9 was repeated with cyclohexane, propionic acid and acetic acid in 250:150:100 volume ratio, 250 psig and 1 percent manganese stearate catalyst. Oxidation at the standard take-up rate, duration and off-gas content was followed with no adjustment for different size of feed molecule or the production of dibasic acid rather than monobasic acid. Oxidate was analyzed in several ways to confirm the production of adipic acid. VPC analysis after esterification with

diazo methane showed adipic acid, cyclo-
hexanol and cyclohexanone present in the
ratios 100:10:5 for a surprising ratio of 7:1
of adipic to intermediates. Several minor
peaks showed on the VPC analysis. In
another analysis technique, raw oxidate was
flashed under vacuum to yield a residue
amounting to 1.8 percent (wt) of the total
which was analyzed by infra red spectros-
copy. This material produced a spectrum
which resembled the reference spectrum for
adipic acid more closely than did a sample
of CP grade adipic acid similarly analyzed.
Actually the VPS presentation of the adipic
acid peak corresponded to CP grade adipic
as to location and retention time and was
extremely distinct and sharp sided indicative
to those skilled in such matters of a material
of extremely high purity. The 1.8 percent
production is considered excellent in view of
the fact that on the basis of hydrocarbon fed
it is actually 3.6 percent. When the 0.5 pro-
duction of cyclohexanol and cyclohexanone
is added to this, it is seen that this conversion
is close to the conversion to cyclohexanone
usually sought in the air oxidation first stage
of the two stage prior art processes. An im-
portant point is that there is no crystalliza-
tion of adipic in the oxidizer or the oxidate
even after it has cooled to room temperature.
Thus there is no problem from this source
comparable to that encountered in conven-
tional adipic acid first stages where adipic
acid formed inadvertently crystallizes out
requiring the use of large quantities of water
in such oxidizers with attendant adverse
effect and numerous problems.

The cyclohexane-adipic acid run including
its analysis provides a graphic illustration of
the commercial significance of the present
invention. Conventional adipic acid plants
generally require plural oxidation stages, the
first air in which the production of cyclo-
hexanol is sought, the latter a nitric acid
oxidation of the cyclohexanol with extremely
complex intervening separation, frequently
involving acids such as boric acid to deliber-
ately produce esters. The present process
per se requires mainly two simple vessels
and a condenser. The first vessel is an oxi-
dizer, the second a flash distillation chamber.
Oxidate flashes in the chamber at a tem-
perature just above the melting point of
adipic acid so that all other materials, acetic
acid, propionic acid, cyclohexane, cyclo-
hexanol, cyclohexanone are vaporized to be
condensed and returned to the oxidizer.
Adipic acids are thus obtained as a liquid
without any solvent or diluent. Removal of
the adipic acid from oxidate is thus so easy
that there is little need for going to high
concentration of acid in oxidate and risking
the higher probability of multiple attack that
ensues. As a practical matter, concentrations
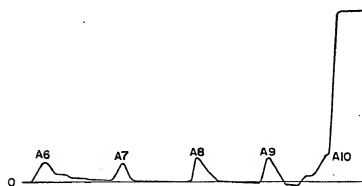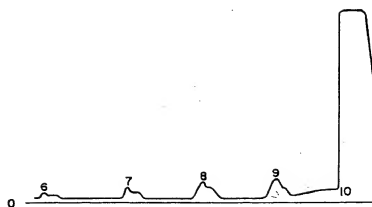of 4 percent, 2 percent or lower are very

practical and any limiting cost as to low
conversion is merely that of operation of
the distillation and of pumping. Another
important point is that the flash vapour is
extremely pure so that cyclohexanol and
cyclohexanone are readily fractionated from
the vapours if it is desired to obtain them for
separate salt. The remaining vapours are the
lower acids of the system, water and cyclo-
hexane. Provison for removal of the water is
desired. By-product CO_2 is also available.

WHAT WE CLAIM IS:—
1. A process for the production of aro-
matic or aliphatic carboxylic acids, which
process comprises oxidising a hydrocarbon
material with an oxidant comprising gaseous
oxygen, in the presence of a mixture of
propionic acid and acetic acid, either added
to the hydrocarbon material or formed in
situ, which mixture forms a single phase
liquid system with the hydrocarbon material.
2. A process as claimed in claim 1,
wherein the oxidation is carried out at a
pressure of from 3 to 25 atmospheres.
3. A process as claimed in claim 1 or
claim 2, wherein the oxidation is carried out
in the presence of a catalytic quantity of a
carboxylate of a heavy metal.
4. A process as claimed in claim 3,
wherein the carboxylate is manganese stear-
ate.
5. A process as claimed in any one of
claims 1 to 4, wherein the oxidation is
carried out with an excess of available
oxygen.
6. A process as claimed in any one of
claims 1 to 5, wherein the hydrocarbon ma-
terial is a pure straight chain hydrocarbon
of a single molecular weight.
7. A process as claimed in any one of
claims 1 to 5, wherein the hydrocarbon ma-
terial is a mixture of straight chain hydro-
carbons of mixed molecular weight averag-
ing about 5 carbon atoms per molecule
higher than the average number of carbon
atoms desired in the product acids.
8. A process as claimed in claim 6 or
claim 7 when carried out at a temperature
of about 115°C.
9. A process as claimed in any one of
claims 1 to 5, wherein the hydrocarbon ma-
terial is a cyclic hydrocarbon or a mixture
of cyclic hydrocarbon.
10. A process as claimed in claim 9,
wherein cyclohexane is oxidised to produce
adipic acid.
11. A process as claimed in claim 9 or
claim 10 when carried out at a temperature
of about 106°C.
12. A process as claimed in any one of
claims 1 to 10, wherein the hydrocarbon
material, the propionic acid, and the acetic
acid are provided in the proportions by
volume of about 25:15:10.

13. A process for producing adipic acid which process comprises oxidizing cyclohexane with an oxidant comprising gaseous oxygen in the presence of a mixture of acetic acid and propionic acid, the mixture forming a single phase liquid system with the cyclohexane, and the volume of the propionic acid present being at least equal to the volume of the acetic acid present, said oxidation being conducted under a pressure of about 3 to 25 atmospheres, and in a temperature limited mode with excess oxygen available, distilling the oxidate under non-oxidizing conditions at a temperature above the melting point of adipic acid to remove cyclohexanol, cyclohexanone and lower boiling materials, recovering the molten adipic acid, and recycling at least a part of the distillate to oxidation.

14. A process as claimed in claim 1 and substantially as hereinbefore described in any one of Examples 1 and 3 to 10.

15. A process as claimed in claim 13 and substantially as hereinbefore described in Example 11.

16. Carboxylic acids when produced by a process as claimed in any one of the preceding claims.

17. Adipic acid when produced by a process as claimed in claim 13 or claim 15.

18. A polymer when produced from adipic acid as claimed in claim 17 and hexamethylene diamine by a condensation reaction.

BOULT, WADE & TENNANT,
111 & 112, Hatton Garden,
London, E.C.1.
Chartered Patent Agents,
Agents for the Applicants.

0 — 6 — 7 — 8 — 9 — 10

0 — A6 — A7 — A8 — A9 — A10

FIG. 2

FIG. I

FIG.1

FIG. 2